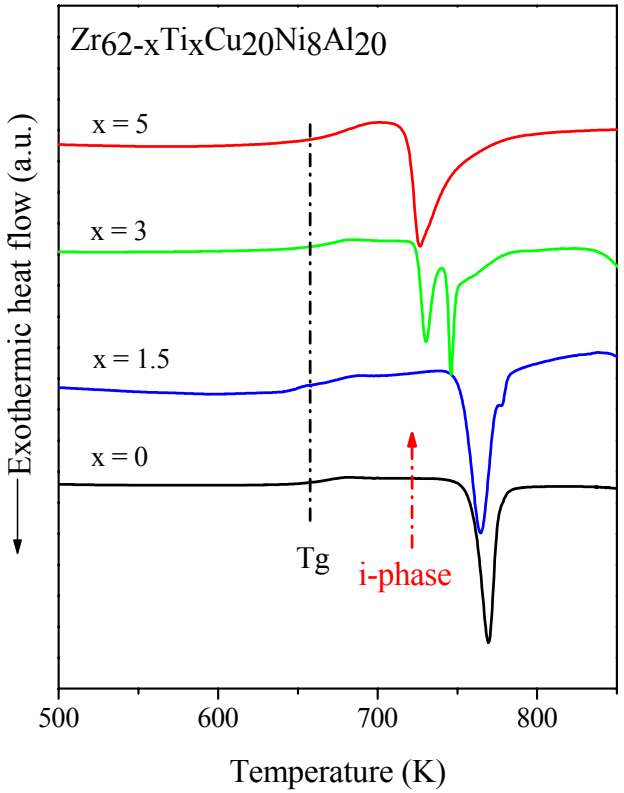
Structural and Microstructural Studies of Ti/Zr and Al-Based Quasicrystals, Approximants, and Metallic Glasses

Kenneth F. Kelton, Washington University, St. Louis, DMR - 0307410

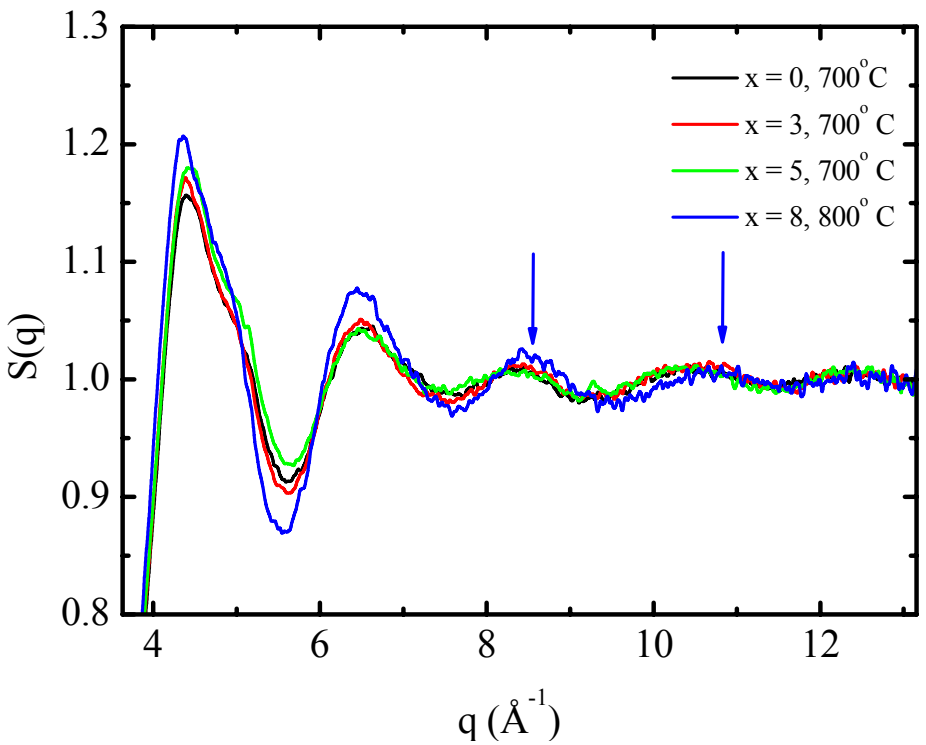
Icosahedral Order and Glass Formation

Icosahedral short range order is frequently invoked to explain glass formation and microalloying



(Fig. 1) Addition of Ti to Zr-Cu-Ni-Al glass enhances glass formation, but to glasses that are less stable due to crystallization of quasicrystal (i-phase) (fig. 1).

L. Q. Xing, Y. T. Shen, K. F. Kelton, Appl. Phys. Lett., **81**, 3371-3373 (2002).



(Fig. 2) S(q) in undercooled liquids of electrostatically levitated $Zr_{62-x}Cu_{20}Ni_8Al_{20}Ti_x$ (see K. F. Kelton et al., Phys. Rev. Lett. 90, 195504-1 (2003) for experimental description). Icosahedral short-range order (ISRO) becomes more perfect with increasing Ti concentration and develops at higher temperature, making crystal nucleation more difficult and enhancing glass formation as observed in fig. 1.

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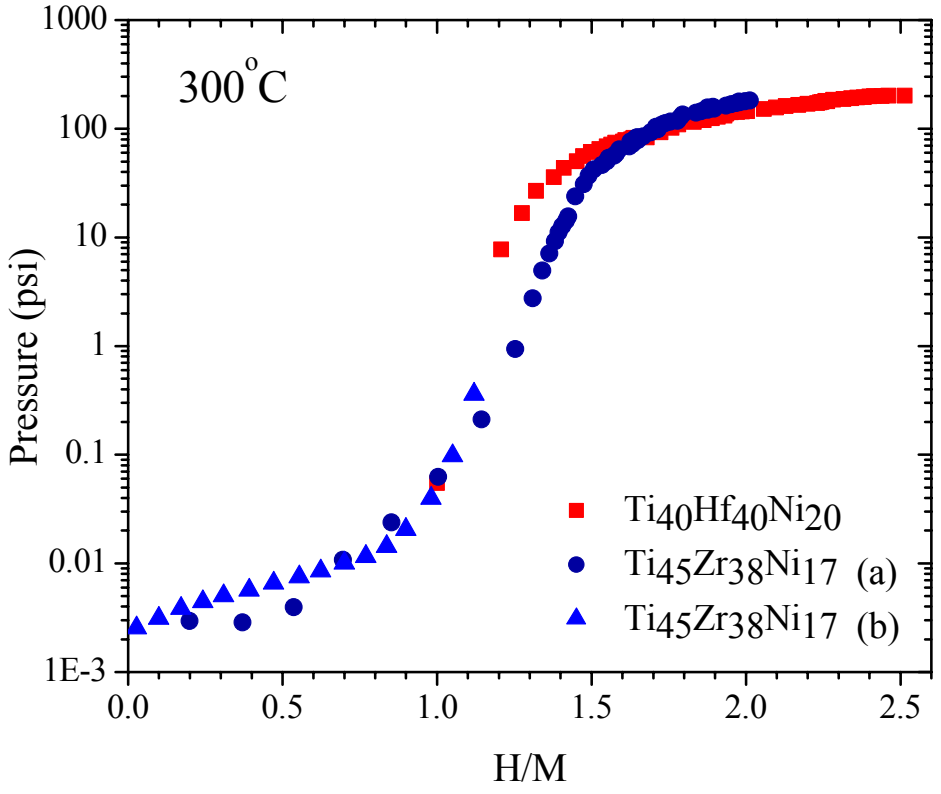
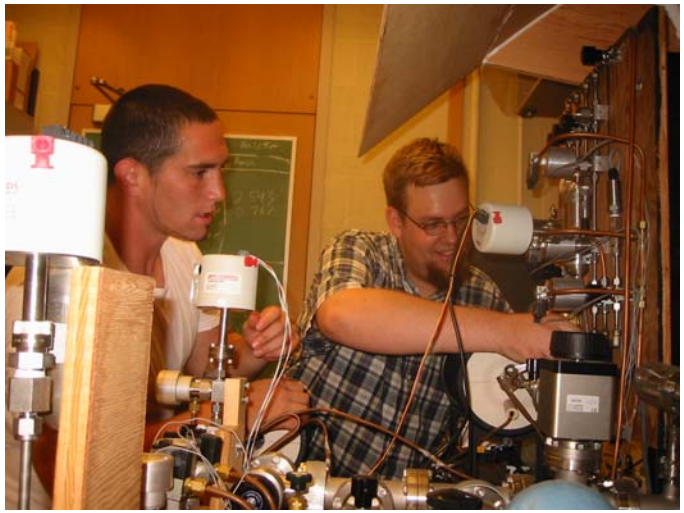


(Fig. 3) – Equilibrium vapor pressures for hydrogen in TiZrNi and TiHfNi measured using a new high pressure apparatus constructed in our group. The reversible high pressure plateau makes these materials promising for hydrogen storage applications. The measurements were made by Van Huett (PhD, summer 2004) Youtao Shen (graduate student) and Josiah Hartzell (undergraduate).

Education:

Undergraduates Drew Newman, Michael George and Josiah Hartzell, graduate students Van Huett, Youtao Shen and Yeonha Sim, and one-half of a postdoc (Li Qian Xing) were supported by this grant.



(Fig. 4) – Undergraduate Josiah Hartzell (right) explains the measurement of the equilibrium vapor pressure of hydrogen in metallic alloys to Michael George.

Outreach:

PI is President of UCSAC, a science advisory council dedicated to improving science education in University City, MO, a racially and socio-economically diverse school system adjacent to Washington University.

First Transparency

Last year under joint NSF and NASA support, we demonstrated growing icosahedral order in undercooled liquids that acts as a template for the nucleation of the icosahedral quasicrystal (K. F. Kelton, G.W. Lee, A. K. Gangopadhyay, R. W. Hyers, T. J. Rathz, J. R. Rogers, M. B. Robinson, D. S. Robinson, Phys. Rev. Lett., **90**, 195504-1 – 195504-4 (2003). Since glass formation is ultimately dependent on the avoidance of significant crystallization during cooling, the growing ISRO can have a dramatic impact on glass formation, if the crystal phases that tend to nucleate during the quench have an incompatible local structure. The nucleation barrier will then increase, rather than decrease, with undercooling, decreasing the nucleation rate during cooling far below the steady-state rate (see figure to the right). The link between ISRO and glass formation is confirmed by our recent x-ray structural studies of a Zr-Cu-Ni-Al-Ti glass as a function of Ti concentration.

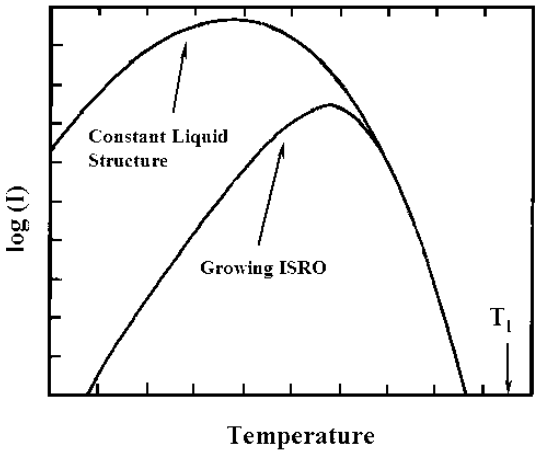


Fig. 1 – Differential scanning calorimetry crystallization studies of ZrTiCuNiAl metallic glasses as a function of Ti concentration. The addition of Ti increases glass formation, but makes the glasses less stable. For Ti concentrations of 3 at.% or higher, the glasses crystallize to icosahedral quasicrystals, suggesting that the enhanced glass formation is due to a developing icosahedral short range order in the liquid/glass.

Fig 2 – Recently obtained measurements of the x-ray structure factors from undercooled ZrTiCuNiAl liquids as a function of Ti concentration. Only the second and higher order peaks in S(q) are shown; the first peak is a measure of the longer range order in the liquid. All liquids show a shoulder on the high-q side of the second peak, indicative of icosahedral order. It becomes more prominent with increasing Ti concentration, however; and the locations of the high order peak agree better with those expected for ideal icosahedral order (blue arrows). Further, the temperatures at which ISRO begins to develop increase with increasing Ti concentration. These observations confirm that ISRO is critical in glass formation for these liquids, and may explain similar features in other liquids/glasses. To our knowledge, this is the first time that this common speculation has been confirmed to this extent in a glass forming system. We have recently discovered a new bulk glass, $Zr_{65}Cu_{27}Ti_8$, that also crystallizes to a quasicrystal, further supporting these ideas.

Second Transparency

This describes the educational aspects and outreach aspects of our research. Three undergraduate students supported by REU funds for this grant are listed. The graduate and post-graduate participants are also listed.

Fig. 3 - Measurements of the hydrogen equilibrium vapor pressure at 300oC in TiZrNi and TiHfNi quasicrystals. Previous measurements had only been made to a pressure of one atmosphere. These new measurement show a prominent plateau-like region with a vapor pressure near 100 psi. The capacity of the TiHfNi quasicrystal at these pressures is approximately 2.5 hydrogen atoms per metal atom (H/M). Our studies show that the samples can reversibly cycle the hydrogen between H/M of 1.5 and 2.5, making them of possible use in hydrogen storage applications. Future work will explore this loading as a function of temperature and microstructure, using nanograins of the quasicrystal synthesized by Akito Takasaki, Japan.

Fig. 4 – Photograph of Josiah Hartzell and Michael George, two undergraduates supported by the REU funds, examining a recently constructed facility for measuring the equilibrium hydrogen vapor pressure in a metal hydride. This higher-pressure unit was constructed to explore the possible uses of Ti/Zr/Hf-based quasicrystals for hydrogen storage applications.

Outreach – The PI is the President of UCSAC, a a science advisory council dedicated to improving science education in University City, MO, a racially and socio-economically diverse school system adjacent to Washington University. This year UCSAC will focus on science in the High School. The High School teachers have requested that scientists give regular seminars on topics of current scientific interest; a schedule has been drawn up and scientists have been recruited. The establishment of a Science Club is planned, with graduate students from research groups also participating in working with the High School Students. These programs are aimed at reaching students who might be interested in science and identifying students who might work in research groups at Washington University. The PI also served as a judge for the Greater St. Louis Science Fair in Spring, 2004.

Notable papers and presentations:

Over the past year, the PI and his group have published a paper in Physical Review Letters and he has had many offers for invited seminars. Notable are:

1. "Difference in Icosahedral Short-Range Order in Early and Late Transition Metal Liquids," G. W. Lee, A. K. Gangopadhyay, K. F. Kelton, R. W. Hyers, T. J. Rathz, J. R. Rogers, and D. S. Robinson, Phys. Rev. Lett., **93**, 037802 (2004).
2. "Influence of Order on the Nucleation Barrier," K. F. Kelton, A. L. Greer, D. M. Herlach, and D. Holland-Moritz, to appear in the MRS Bulletin.
3. "Coupled Processes in Nucleation, K. F. Kelton, Invited Speaker at the 106th Annual Meeting of the American Ceramic Society, 18-21 April, 2004, Indianapolis, IN.
4. "Getting the Hot Structures," K. F. Kelton, Plenary Lecture at the 2004 Denver X-ray Conference, 2-6 August, 2004, Steamboat Springs, CO.
5. "Amorphous Metal Formation and Crystallization – Coupled Processes in Crystal Nucleation," K. F. Kelton, Keynote Lecture ISMANAM 2004, 22-26 August, 2004, Sendai, Japan.